

# PATENT SPECIFICATION

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## (54) A PROCESS FOR PRODUCING ELASTIC FOAM MOULDED ARTICLES

(71) We, ASAHI KASEI KOGYO KABUSHIKI KAISHA, a Corporation organised under the Laws of Japan, of 25-1 Dojima-hamadori-1-chome, Kita-ku, Osaka, Japan,

5 do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 The present invention relates to a novel process for producing elastic foamed articles by moulding.

A moulded article of a rubber-like material which is highly elastic at normal 15 temperature is a useful product having a wide field of application as a cushioning material for purposes such as furniture, bedding and automobile parts.

A known process for producing a foamed 20 body of thermoplastic resin, in particular polystyrene is the so-called bead foaming process (see, for example United States Patents Nos. 2,744,291 and 2,787,809). In the known bead foaming process, poly- 25 styrene pellets or beads containing a low-boiling compound such as propane, butane, pentane or neopentane are heated to effect a preliminary foaming, and the resultant granular preliminarily foamed bodies are 30 heated in a mould to effect further foaming and expansion. The expanded granular foamed bodies coalesce mutually to form a unitary moulded article.

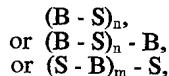
However, such a bead foaming process is 35 applicable only to a polystyrene resin; application of the process to the other resins has not yet been accomplished successfully.

Foamed polystyrene articles produced by the said bead foaming process are poor in 40 elasticity, while known elastic foamed polyurethane and foamed polyethylene are difficult to mould. Further, in the case of foamed rubber, moulding is complicated and in particular the moulding of complex 45 shapes has been impossible to perform since

a vulcanizing step and a foaming step should be carried out simultaneously.

One of the objects of the present invention is to provide a relatively simple process for producing moulded elastic foamed 50 articles, which may be of complex shapes.

In accordance with the present invention a process for producing an elastic foam moulded article comprises extruding under pressure and at elevated temperature 55 through holes a fluid foaming mixture obtained by mixing (1) 100 parts by weight of a thermoplastic elastomeric block copolymer (referred to hereinafter as the block copolymer for short) represented by the formula 60



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wherein B represents substantially a 1,3-butadiene polymer block (referred to herein-after as the butadiene polymer block), S represents substantially a styrene polymer block, n is an integer of 2 to 10 and m is an 70 integer of 1 to 10, the copolymer having a molecular weight of 10,000 to 500,000 and a styrene content of 10 to 70% by weight, or a mixture of such block copolymers (2) 25 to 300 parts by weight of polystyrene, and 75 (3) 0.1 to 100 parts by weight of a foaming agent which is an organic compound having a boiling point lower than the softening temperature of the polystyrene, cutting the resultant extruded mixture into segments 80 while the same is still soft and not yet completely expanded, allowing the resultant segments to foam and expand, cooling the foamed and expanded segments to form granules, filling the granules into a closable 85 but not air-tight mould, and heating the granules therein to a temperature at which they soften and further foam and expand.

In the formula for the block copolymer, if n were 1 the product would not be an 90

elastomer unless vulcanization were effected, whereas if  $n$  were more than 11, the strength and the elastic elongation of the product would be poor. Further, if  $m$  were 0, an elastomer would not be obtained whereas if  $m$  were more than 11 the elastomeric properties of the product would be poor.

The molecular weight of the block copolymer is preferably 20,000 to 200,000 and it preferably contains 20 to 50% by weight of styrene. A block copolymer having a molecular weight less than 10,000 is insufficient in strength while one having a molecular weight of more than 500,000 is difficult to extrude. Further, a styrene content of less than 10% by weight results in a low tensile strength and too low a hardness, while more than 70% by weight although it gives high strength, gives too low an elongation so that the elastomeric properties are poor.

A portion of the styrene in the block copolymer may be replaced with other vinyl-substituted aromatic compounds, for example, vinyl toluene, dimethyl styrene or  $\alpha$ -methyl styrene.

The block copolymer specified has an elasticity like that of vulcanized rubber at normal temperature and is plastic at an elevated temperature. Within the limits specified the block polymer may be selected to have the elasticity desired for the product and a plasticity at elevated temperature suitable for the foaming step.

As regards the polystyrene content, less than 25 parts by weight of polystyrene per 100 parts by weight of the block copolymer would result in poor foaming efficiency and would be apt to cause bubbles which inter-communicate in the direction of extrusion. Further, the resultant granular foamed bodies would not produce a commercially useful moulded article. On the other hand, the use of more than 300 parts by weight of the polystyrene would give a foamed article having properties akin to those of a foamed polystyrene article i.e. an article having insufficient elasticity.

Any foaming agent useful for extrusion foaming of polystyrene may be used. For example, there are available low-boiling hydrocarbons such as pentane, butane, and propane, and halogenated hydrocarbons such as methyl chloride, dichlorodifluoromethane and dichlorotetrafluoroethane. The amount employed may vary within the specified range, depending upon the kind of foaming agent used and the ratio between the block copolymer and the polystyrene. It is preferred to use 1 to 70 parts by weight, based on 100 parts by weight of the block copolymer.

For mixing the foaming agent, any conventional technique employed in an extrusion foaming process may be used. That is to say, the foaming agent may be fed

directly under pressure into a mixture of the block copolymer and polystyrene charged into a screw type extruder, or the polystyrene or the block copolymer may be impregnated in advance. In the latter case, the polystyrene is preferred as the component to be impregnated with the foaming agent. The foaming agent could be incorporated into the block copolymer, but since the rate of vaporization of the foaming agent from the block copolymer is high and handling after the impregnation may be delayed, incorporation into the block copolymer is not preferred. Commercially available foamable polystyrene beads may be used as the polystyrene impregnated with the foaming agent.

As an agent for controlling the size of the bubbles in the foamed body generated in the extrusion-foaming, the use of a small amount of an inorganic powder, a carbon dioxide gas generating agent or other heat sensitive gas generating agents is efficacious to form fine and uniform bubbles. Examples are calcium carbonate, sodium carbonate, magnesium carbonate, silicic acid, clay, talc, zinc oxide and boric acid.

Further, for regulating extrusion-processability and physical properties, a process oil as used as an additive for rubber may be added. For example, naphthenic process oils form a petroleum fraction, and paraffinic process oils may be mentioned. The amount thereof is generally 1 to 50 parts by weight on the basis of 100 parts by weight of the block copolymer.

Furthermore, for modifying physical properties of the product a small amount of filler as used as an additive for rubber may be added. Examples thereof are zinc white (zinc oxide), calcium carbonate and silicic acid. Some of these may serve the dual purposes of bubble size regulation and modification of product properties.

Before the mixture extruded through holes has fully foamed, and while still soft, the extruded strands are cut into segments, for instance continuously at constant intervals by a knife-like device which rotates or reciprocates in the neighbourhood of the extrusion orifice outlets. Since the resultant segments are still soft they transform into a ball-like shape while continuing foaming and expansion. They are then cooled, forming foamed granules having a smooth surface.

For producing a moulded article from the foamed granules, a known bead foaming technique for producing a moulded foamed article from foamable beads may be used. That is to say, by filling the foamed granules into a mould capable of closing but not making air-tight and heating the granules by a hot medium such as steam, water or air to soften them, vapour contained in the bubbles in the granules is expanded and the granules themselves are

thereby swelled to fill the mould. Further, the granules coalesce and form a unitary moulded article having a shape conforming to that of the mould.

5 The moulded article thus obtained develops favourable elasticity by leaving it for a time after cooling. The time of leaving varies depending upon the size of the article. That is to say, the larger the article, the 10 longer is the leaving time required. That is because, when the article which has been produced by heating, foaming and expanding the foamed granules is cooled, vapour in the bubbles which constitute the article 15 contracts and reduces the pressure in the bubbles. Therefore, if at this time the article is deformed by an external force, a reactive force capable of restituting the deformation does not act and so the deformation 20 remains as a permanent deformation. However, by leaving the article for a time before subjecting it to deformation, the pressure in the bubbles becomes atmospheric, and in consequence a favourable 25 restituting property of the article is developed by a combination of the force of compression of the vapour in the bubbles and the elastic resilience of the resinous composition itself.

30 The present process is suitable for producing moulded articles of any desired size and shape; for instance, shock absorbers for transportation, such as for automobiles and aeroplanes; cushioning elements for packaging; fenders; fender beams; boats; floats; buoys; shoe soles; sporting goods; saddles; grips; gaskets; artificial leather; heat insulators; pads; cushions for sofas and chairs; hoses; toys; and flexible packages.

35 40 The following Examples illustrate the present invention.

*Example 1*

100 parts by weight of polystyrene pellets 45 having a melt index of 3 (ASTM D 1238-57T, condition G) were mixed with 100 parts by weight of a block copolymer (1) shown in Table 1, which had been copolymerized using n-butyl lithium as a catalyst. 0.5 part 50 by weight of talc was mixed with 100 parts by weight of the resultant mixed solid and the resultant mixture was fed to a screw type extruder. 7 parts by weight of dichlorodifluoromethane per 100 parts by 55 weight of the fed solid component were fed under pressure to the resultant mixture through a mixer connected to one end of the screw type extruder and were mixed well. The resultant mixture was extruded 60 through a die having fine holes which was located at the other end of the extruder. The mixture became fluid by being heated in the extruder in the vicinity of the die. The extruded soft strands were cut at a 65 constant interval by a knife which rotated

at a velocity of 140 r.p.m. in a plane parallel to the face of the die and spaced not more than 1 mm therefrom, the resulting soft segments being allowed to foam and expand, and then being allowed to cool. Small 70 spheroidal foamed granules were obtained having a uniform size of 3 mm average diameter and a smooth surface. They were 0.061 Kg/l in density and had uniform bubbles having an average bubble diameter 75 of 0.9 mm.

When one of these foamed granules was boiled in boiling water for one minute, it swelled to a diameter of about 4 mm and did not contract even when it was taken out 80 from the boiling water and cooled. The granule was then left as it was for one day and night and developed high elasticity. The density of the resultant granule was 0.033 Kg/l and the uniform bubbles thereof had 85 an average bubble diameter of 1.1 mm.

Further, when the granules were filled into a closable but not air-tight mould, left for 3 minutes therein in a steam atmosphere having a pressure of 0.4 Kg/cm<sup>2</sup>, and the 90 product was then removed from the mould, the granules had coalesced and further expanded to produce a moulded article which exactly conformed to the mould. The moulded article developed extremely high 95 elasticity after 2 days.

*Example 2*

100 parts by weight of naphthenic process oil were mixed with 100 parts by weight of a block copolymer (11) shown in Table 1 which had been copolymerized using n-butyl lithium as a catalyst. 50 parts by weight of polystyrene pellets having a melt index of 0.5 (ASTM D 1238-57T, condition G) and 1.5 parts by weight of talc were mixed to the resultant mixture. The resultant mixture was fed to the same extruder as in Example 1. 14 parts by weight of dichlorotetrafluoroethane per 100 parts by weight of the resultant solid component were fed in under pressure and mixed therewith, and the mixture was extruded and cut in the same manner as in Example 1, forming foamed 110 granules having an average diameter of 4 mm. The density of the granules was 0.070 Kg/l and the uniform bubbles thereof had an average bubble diameter of 0.5 mm. 115

When the granules were filled into a closable but not air-tight mould, left for 2 minutes in a steam atmosphere having pressure of 0.4 Kg/cm<sup>2</sup> and the product removed, it was found to be a unitary moulded article which exactly conformed to the mould. The density of the moulded article was 0.043 Kg/l and it had an average bubble diameter of 0.6 mm. The moulded article developed extremely high elasticity after 120 leaving it for 3 days.

**Example 3**

10 parts by weight of calcium carbonate rubber filler were mixed with 100 parts by weight of a block copolymer (III) shown 5 in Table 1. 200 parts by weight of polystyrene pellets having a melt index of 9 (ASTM D 1238-57T, condition G) and 0.05 part by weight of talc were mixed with the first mixture. The resultant mixture was 10 fed to the same extruder as in Example 1. Four parts by weight of methyl chloride per 100 parts by weight of the resultant solid component were fed in under pressure and mixed therewith, and the mixture was ex-

truded and cut in the same manner as in 15 Example 1, forming foamed granules having an average diameter of 5 mm. The density of the granules was 0.065 Kg/l and they had an average bubble diameter of 0.8 mm.

When the granules were filled into a 20 closable but not air-tight mould, heated with water at a temperature of 90°C for 3 minutes and the product removed, it was found to be a unitary moulded article. This article developed extremely high elasticity after 4 25 days. The density of the moulded article was 0.040 Kg/l and it had an average bubble diameter of 1.1 mm.

**Table 1**

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*Composition and physical properties of block copolymers*

|  | Block copolymer (I)     | Block copolymer (II) | Block copolymer (III)         |
|--|-------------------------|----------------------|-------------------------------|
| 35 Composition of block *                                | B - S - B - S           | S - B - S            | B - S - B - S - B             |
| Molecular weight of each block                           | 12000-18000-43000-18000 | 29000-60000-27000    | 12000-25000-25000-25000-13000 |
| Styrene content (% by weight) (refractive index process) | 40                      | 50                   | 50                            |
| 40 Tensile strength (Kg/cm <sup>2</sup> ) (JIS K-6301)   | 195                     | 190                  | 190                           |
| Elongation (%) (JIS K-6301)                              | 1000                    | 700                  | 800                           |
| 45 Hardness (JIS K-6301)                                 | 80                      | 95                   | 90                            |
| Melt Index (ASTM D-1238-57T, condition G)                | 2.5                     | 3.8                  | 4.5                           |

50 Remark: \* B signifies polybutadiene block and S signifies polystyrene block.

**WHAT WE CLAIM IS:—**

1. A process for producing an elastic foam moulded article, which comprises extruding under pressure and at elevated temperature 55 through holes a fluid foaming mixture obtained by mixing (1) 100 parts by weight of a thermoplastic elastomeric block copolymer represented by the formula

60 (B - S)<sub>n</sub>,  
or (B - S)<sub>n</sub> - B,  
or (S - B)<sub>m</sub> - S,

wherein B represents substantially a 1,3-65 butadiene polymer block, S represents substantially a styrene polymer block, n is an integer of 2 to 10 and m is an integer of 1 to 10, the copolymer having a molecular weight of 10,000 to 500,000 and a styrene content of 10 to 70% by weight, or a mixture of such block copolymers, (2) 25 to 300 parts by weight of polystyrene, and (3) 0.1 to 100 parts by weight of a foaming agent which is an organic compound having a boiling point lower than the softening temperature 75

ture of the polystyrene, cutting the resultant extruded mixture into segments while the same is still soft and not yet completely expanded, allowing the resultant segments to foam and expand, cooling the foamed and expanded segments to form granules, filling the granules into a closable but not air-tight mould and heating the granules therein to a temperature at which they soften and further foam and expand.

80 2. A process in accordance with Claim 1 wherein the thermoplastic elastomeric block copolymer has a molecular weight of 20,000 to 200,000 and a styrene content of 20 to 50% by weight.

85 3. A process in accordance with Claim 1 or Claim 2 wherein the foaming agent is methyl chloride, dichlorodifluoromethane or dichlorotetrafluoroethane.

90 4. A process in accordance with any of the preceding claims wherein a process oil is added to the foaming mixture.

95 5. A process in accordance with any of the preceding claims wherein a filler for rubber is added to the foaming mixture.

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6. A process in accordance with any of the preceding claims wherein an agent for regulating bubble size is added to the foaming mixture.

5 7. A process in accordance with Claim 6 wherein the agent for regulating bubble size is talc.

8. A process for producing an elastic foam moulded article, substantially as described in any of the Examples.

9. Moulded articles which have been produced by a process as claimed in any of the preceding claims.

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